Dimethylglyoxime and related compounds of cobalt have been invoked widely as vitamin B_{12} analogues.[6,21] The relatively low Co–C bond dissociation energies identified in these studies are consistent with and supportive of the proposed role of Co–C bond homolysis in coenzyme B_{12} promoted reactions.[4-6] Our results also serve to identify some of the factors that influence Co–C bond dissociation energies in such compounds and which may, thus, be involved in promoting the Co–C bond homolysis step.

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Registry No. py(DH)$_2$Co-CH(CH$_3$)C$_6$H$_5$, 37824-58-1; 4-NH$_2$-py-(DH)$_2$Co-CH(CH$_3$)C$_6$H$_5$, 80227-63-0; 4-CH$_3$-py(DH)$_2$Co-CH-(CH$_3$)C$_6$H$_5$, 80227-64-1; 4-CN-py(DH)$_2$Co-CH(CH$_3$)C$_6$H$_5$, 80227-65-2; Im(DH)$_2$Co-CH(CH$_3$)C$_6$H$_5$, 80227-66-3.

(21) Halpern, J. *Ann. N. Y. Acad. Sci.* **1974**, *239*, 2 and references therein.

Kinetic Determination of Transition-Metal–Alkyl Bond Dissociation Energies: Application to Organocobalt Compounds Related to B_{12} Coenzymes

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Despite their widespread significance for various organometallic, biochemical, and catalytic processes,[1] few transition-metal–alkyl bond dissociation energies have been determined reliably, reflecting in considerable degree the limited applicability of the methods available for such determinations.[2,3] The studies described in this communication reveal conclusively that the thermal decomposition of certain organocobalt compounds proceeds via homolytic cobalt–carbon bond dissociation and demonstrate that the dissociation energies of such bonds can be deduced from kinetic measurements. Interest in the results of these studies is enhanced by the relevance of these organocobalt compounds as coenzyme B_{12} analogues[4,5] and by the further potential of the method for the determination of other transition-metal–alkyl bond dissociation energies.

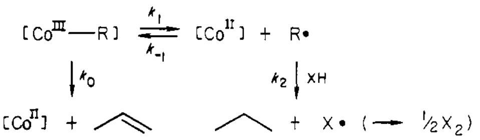
Our studies relate to the thermal decompositions of organocobalt Schiff base compounds [py(saloph)Co–R] (where py = pyridine, saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamine and R = alkyl or benzyl), which were found to proceed at conveniently measurable rates in pyridine solution[6] at temperatures below 100 °C in the presence of an efficient radical trap such as the hydrogen donor, *n*-$C_8H_{17}SH$ (abbreviated XH). When R = *n*-propyl or isopropyl (i.e., an alkyl containing a β hydrogen), the reaction yielded a mixture of propene and propane, exhibiting the kinetics and product distribution corresponding to Scheme I where [$Co^{III}R$] = [py(saloph)Co–C_3H_7] and [Co^{II}] = [py(saloph)Co^{II}].[7,8]

Table I. Product Distribution from the Decomposition of [py(saloph)Co–CH(CH$_3$)$_2$] at 62.7 °C in Pyridine Solution Containing 1.3 × 10^{-3} M [Co^{II}]

$10^3[n\text{-}C_8H_{17}SH]$, M	$10^3 k_{obsd}$, s^{-1}	$(C_3H_6)_{calcd}$,^{a} %	$(C_3H_6)_{obsd}$, %
0	1.4	72	71
1.9	3.3	30	27
3.8	5.0	20	17
5.8	6.5	15	12
9.6	9.6	10	8

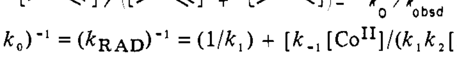
^{a} Percent $(C_3H_6)_{calcd} = (100k_0/k_{obsd})$ where $k_0 = 1.00 \times 10^{-3}$ s^{-1}.

Scheme I



According to Scheme I, the kinetics of the reaction should conform to eq 1 and the product distribution to eq 2. Kinetic measurements,[10] typically encompassing the initial concentration ranges ca. 5 × 10^{-4} M CoR, 0–2 × 10^{-3} M Co^{II}, and 0–2 × 10^{-2} M *n*-$C_8H_{17}SH$, yielded excellent linear plots (Figure 1) of $(k_{RAD})^{-1}$ vs. [Co^{II}] and $(k_{RAD})^{-1}$ vs. $[C_8H_{17}SH]^{-1}$, in accord with eq 3, which is derived by rearrangement of eq 1 (k_{RAD} corresponding to the contribution to the overall rate constant of the free radical path initiated by the Co–R bond homolysis step, i.e., k_1).

$$\frac{-\mathrm{d}\ln[\mathrm{Co^{III}R}]}{\mathrm{d}t} = k_{obsd} = k_0 + \frac{k_1 k_2[\mathrm{XH}]}{k_{-1}[\mathrm{Co^{II}}] + k_2[\mathrm{XH}]} \qquad (1)$$



(2)

$$(k_{obsd} - k_0)^{-1} = (k_{RAD})^{-1} = (1/k_1) + [k_{-1}[\mathrm{Co^{II}}]/(k_1 k_2[\mathrm{XH}])] \qquad (3)$$

Values of k_0 were determined by extrapolation of k_{obsd} to limiting high Co^{II} (and low XH) concentrations, and values of k_1 and k_{-1}/k_2 were deduced from the intercepts and slopes of plots exemplified by those in Figure 1. Table I records the excellent agreement that was obtained between the observed product distribution and that calculated from the rate data according to eq 2. For R = neopentyl or benzyl (i.e., lacking a β hydrogen), the olefin-producing path was absent; accordingly, the organic products were exclusively neopentane and toluene, respectively, and the kinetics conformed to eq 1 and 3, with $k_0 = 0$. The results of the kinetic measurements are summarized in Table II which also lists activation parameters derived from the temperature dependence, measured at three to five temperatures over a 10–20 °C interval (43–63 °C for R = isopropyl; 77–97 °C for *n*-propyl; 54–69 °C for neopentyl; 55–65 °C for benzyl).[10]

The kinetic behavior and product distribution clearly establish the validity of Scheme I and define the kinetics of the cobalt–carbon bond homolysis step corresponding to k_1. The mechanism of the olefin-elimination step corresponding to k_0 is less clear. While a "concerted"[9,11] elimination cannot be ruled out, a more likely pathway appears to be that depicted by eq 4, i.e., β-hydrogen

$$[\mathrm{Co^{III}\text{–}C_3H_7}] \rightarrow \overline{[\mathrm{Co^{II}}],\mathrm{C_3H_7}\cdot} \rightarrow \mathrm{C_3H_6} + [\mathrm{CoH}] \rightarrow \mathrm{C_3H_6} + [\mathrm{Co^{II}}] + {}^1/{}_2\mathrm{H_2} \qquad (4)$$

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(1) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171 and references therein.

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(3) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124.

(4) Halpern, J. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 2 and references therein.

(5) Halpern, J. In "Vitamin B_{12}"; Dolphin, D., Ed.; Wiley: New York, in press.

(6) Pyridine was used as solvent to eliminate complications due to possible dissociation of the axially coordinated pyridine ligand.

(7) Qualitatively similar results were obtained for organocobalt complexes of other Schiff bases including *N,N'*-bis(salicylidene)ethylenediamine (salen) and bis(acetylacetone)ethylenediamine (bae) and using other radical traps including 1,4-cyclohexadiene, R_3SnH, and copper(II).

(8) Our *demonstration* that [py(saloph)Co–CH(CH$_3$)$_2$] decomposes predominantly via homolytic Co–C bond cleavage contrasts with the assertion[9] that isopropylcobalamin decomposes by a concerted olefin elimination path.

(9) (a) Grate, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1979**, *101*, 4601. (b) Schrauzer, G. H.; Grate, J. H. *Ibid.* **1981**, *103*, 541.

(10) The kinetics were monitored spectrophotometrically, following the disappearance of [CoR], at ca. 650 nm. The quantitative conversion of CoR to Co^{II} was confirmed spectrophotometrically. The organic products, i.e., propene, propane, neopentane, toluene, and $(n\text{-}C_8H_{17}S)_2$ were determined by VPC and found to conform to the reported stoichiometry. Except where otherwise noted, the precision of the measured kinetic parameters is estimated to be rate constants, ±5%; ΔH^*, ±1kcal/mol; ΔS^*, ±3 cal/mol·K.

(11) Duong, K. N. V.; Ahond, A.; Merienne, C.; Gaudemer, A. *J. Organomet. Chem.* **1973**, *55*, 375.

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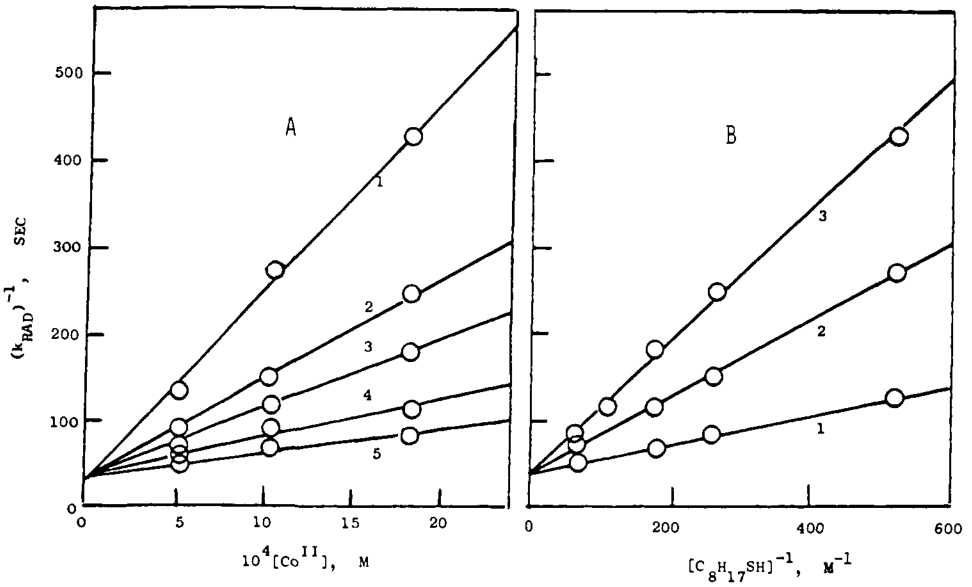

Figure 1. Kinetics of the decomposition of $[py(saloph)Co\text{-}CH(CH_3)_2]$ at 62.7 °C in pyridine solutions containing $n\text{-}C_8H_{17}SH$. (A) $10^3[n\text{-}C_8H_{17}SH]$, M: 1, 1.9; 2, 3.8; 3, 5.8; 4, 9.6; 5, 15.4; (B) $10^4[py(saloph)Co^{II}]$, M: 1, 5.0; 2, 10.3; 3, 18.5.

Table II. Summary of Kinetic Data

R	k_0(70 °C), s^{-1}	$\Delta H^{\ddagger}_0$, kcal/mol	$\Delta S^{\ddagger}_0$, cal/mol·K	k_1(70 °C), s^{-1}	$\Delta H^{\ddagger}_1$, kcal/mol	$\Delta S^{\ddagger}_1$, cal/mol·K	$(k_{-1}/k_2)_{70\,°C}$	$D_{Co\text{-}R}$, kcal/mol
$CH_2CH_2CH_3$	1.0×10^{-5}	23.4	−15.1	4.7×10^{-4}	27.1 ± 1.1	2.6	10	25
$CH(CH_3)_2$	1.9×10^{-3}	19.8	−15.5	5.7×10^{-2}	21.8 ± 1.0	−2.9	93	20
$CH_2C(CH_3)_3$				3.4×10^{-2}	20.3 ± 0.6	−6.2	8	18
$CH_2C_6H_5$				1.2×10^{-2}	23.6 ± 1.0	1.3	70	22

transfer between the $\overline{C_3H_7\cdot, Co^{II}}$ geminate radical pair, followed by rapid decomposition of the resulting cobalt hydride. Such β-hydrogen abstraction has been shown to be fast in closely related systems[1,12] and, in one case, to occur within the cage lifetime of such a geminate radical pair.[12] In any event, since k_0 is small compared with k_1 (in no case greater than ca. 3%), its significance, even in those cases where some olefin formation does occur, does not seriously affect the interpretation of the major k_1-derived radical pathway.

Recombination of cobalt(II) complexes with alkyl radicals has previously been demonstrated to be diffusion controlled.[1,13] Our results provide direct confirmation of this in the present systems. The values of ca. 10–10^2 for k_{-1}/k_2 in Table II, in combination with earlier estimates of k_2 (ca. 10^7 M^{-1} s^{-1} at ambient temperatures),[14] yield values of ca. 10^8–10^{10} M^{-1} s^{-1} for k_{-1}, i.e., close to the diffusion-controlled limit. Assuming $\Delta H^{*}_{-1} \sim 2$ kcal/mol for such a diffusion-controlled process permits the Co–R bond dissociation energy, $D_{Co\text{-}R}$, to be deduced reliably from the measured values of ΔH^{*}_1, i.e., $D_{Co\text{-}R} \sim \Delta H^{*}_1 - 2$ kcal/mol.[15]

Values of $D_{Co\text{-}R}$ obtained in this way are listed in Table II. The values span the range 18–25 kcal/mol. While the trend, in part (e.g., n-propyl > benzyl), parallels that for other alkyl bond dissociation energies (e.g., R–H), the low values of $D_{Co\text{-}R}$ for isopropyl and neopentyl, compared with benzyl, attest to the importance of steric effects in such a cobalt complex, an inference underscored by the results of structural investigations on related organocobalt compounds.[15] In this context, our results suggest that neopentyl is at least as sterically demanding as isopropyl. The unusual reactivities reported recently for certain neopentylplatinum compounds also may reflect such sterically induced destabilization.[17]

On the basis of a variety of criteria,[4] Schiff base cobalt complexes probably represent some of the closest analogues thus far identified (notably in respect of the apparent stabilities of organocobalt derivatives) of the corresponding vitamin B_{12} derivatives. The $D_{Co\text{-}R}$ values in Table II, which we thus believe to be close to those of the corresponding cobalamins, lie in a range appropriately low so as to be consistent with the proposed role of cobalt–carbon bond homolysis in coenzyme B_{12}-promoted reactions.[4,5,18,19] Our results also reinforce the view that steric factors may play an important role in promoting this bond homolysis.

Compared with another method that we have recently described[3] for determining transition-metal–alkyl bond dissociation energies (and applied to some other organocobalt compounds), the present approach would appear to have much wider applicability. We are currently extending our measurements to other transition-metal–alkyl compounds including organocobalamins and organomanganese compounds.

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Registry No. py(saloph)Co-$CH_2CH_2CH_3$, 80105-87-9; py(saloph)-Co-$CH(CH_3)_2$, 80105-88-0; py(saloph)Co-$CH_2C(CH_3)_3$, 80105-89-1; py(saloph)Co-$CH_2C_6H_5$, 80105-90-4.

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(15) This approach parallels that invoked recently to estimate cobalt–carbon bond dissociation in certain benzyl- and secondary alkylcobalamins.[9b] The latter studies, however, did not verify the proposed homolytic dissociation pathway by establishing the full kinetics of the radical competition scheme.

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